TRANSMITTAL LETTER TO THE UNITED STATES — ATTORNEY'S DOCKET NUMBER 48320

DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371 — U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP 98/05469	28 August 1998	8 September 1997

TITLE OF INVENTION: IMPREGNATED SALTS, A METHOD FOR PRODUCING SAID SALTS, AND THE USE OF THE SAME

APPLICANT(S) FOR DO/EO/US Ulrich BROECKEL, Bruno KAESLER, Guenter GAUS, Joachim MEYER

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. /X/ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.

2. / / This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.

3. /X/ This express request to begin national examination procedures (35 U.S.C.371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).

4. /x / A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5. /X/ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).

   a./X/ is transmitted herewith (required only if not transmitted by the International Bureau).
   b./ / has been transmitted by the International Bureau.
   c./ / is not required, as the application was filed in the United States Receiving Office (RO/US0).

6. /X/ A translation of the International Application into English (35 U.S.C. 371(c)(2)).

7. / / Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).

   a./ / are transmitted herewith (required only if not transmitted by the International Bureau).
   b./ / have been transmitted by the International Bureau.
   c./ / have not been made; however, the time limit for making such amendments has NOT expired.
   d./ / have not been made and will not be made.

8. / / A translation of the amendments to the claims under PCT Article 19(35 U.S.C. 371(c)(3)).

9. /X/ An oath or declaration of the inventor(s)(35 U.S.C. 171(c)(4)).

10./ / A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11./X/ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.

12./X/ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.

13./X/ A FIRST preliminary amendment.
/ / A SECOND or SUBSEQUENT preliminary amendment.

14./ / A substitute specification.

15./ / A change of power of attorney and/or address letter.

16./X/ Other items or information.
International Search Report
International Preliminary Examination Report

09/487000

U.S. Appln. No. (If known)	INTERNATIONAL APPLN. NO. PCT/EP 98/05469	ATTORNEY'S DOCKET NO. 48320

17. /X/ The following fees are submitted	CALCULATIONS	PTO USE ONLY
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO.....$840.00	840.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482).....$750.00		
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)).....$700.00		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....$ 970.00		
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied pro-visions of PCT Article 33(2)-(4).....$96.00		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 840.00	
Surcharge of $130.00 for furnishing the oath or declaration later than / / 20 / /30 months from the earliest claimed priority date (37 CFR 1.492(e)).		

Claims	Number Filed	Number Extra	Rate		
Total Claims	16	-20	X$18.		
Indep.Claims	1	-3	X$78.		
Multiple dependent claim(s)(if applicable)			+270.		
TOTAL OF ABOVE CALCULATION			=	840.00	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).					
SUBTOTAL			=	840.00	
Processing fee of $130. for furnishing the English translation later than / /20 / /30 months from the earliest claimed priority date (37 CFR 1.492(f)). +					
TOTAL NATIONAL FEE			=	840.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) $40.00 per property			=	40.00	
TOTAL FEES ENCLOSED			=	$ 880.00	

Amount to be refunded: $

Charged $

a./X/ A check in the amount of $ 880. to cover the above fees is enclosed.

b./ / Please charge my Deposit Account No. _____ in the amount of $_____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c./X/ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0345. A duplicate copy of this sheetis enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b) must be filed and granted to restore the application to pending status.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of)
BROECKEL et al.) BOX PCT
)
International Application)
PCT/EP 98/ 05469)
)
Filed: August 28, 1998)
)

For: IMPREGNATED SALTS, A METHOD FOR PRODUCING SAID SALTS, AND THE USE OF THE SAME

PRELIMINARY AMENDMENT

Honorable Commissioner of
Patents and Trademarks
Washington, D.C. 20231

Sir:

Prior to examination, kindly amend the above-identified application as follows:

IN THE CLAIMS

Claim 3, line 1, delete "or 2".

Claim 4, line 1, delete "any of claims 1 to 3" and insert --claim 1--.

Claim 5, line 1, delete "any of claims 1 to 4" and insert --claim 1--.

Claim 8, line 1, delete "or 7".

Claim 9, line 1, delete "any of claims 6 to 8" and insert --claim 6--.

Claim 10, line 1, delete "any of claims 6 to 9" and insert --claim 6--.

Claim 11, line 1 delete "any of claims 6 to 10" and insert --claim 6--.

Claim 14, lines 2 and 3, delete "as claimed in claim 1".

Claim 16, line 2, delete "as claimed in claim 6" .

REMARKS

The claims have been amended to eliminate multiple dependency and to put them in better form for U.S. filing. No new matter has been added.

Favorable action is solicited.

Respectfully submitted,

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Impregnated salts, their production and their use

The present invention relates to impregnated salts comprising at least one salt of one or more carboxylic acids, which salt has been impregnated with from 0.5 to 30% by weight, based on the carboxylic acid salt, of at least one carboxylic acid, and to preservatives comprising an impregnated salt and, where appropriate, at least one carrier and/or formulation auxiliaries, it being possible for the preservatives to be coated with a protective agent and/or a dusting powder.

The invention furthermore relates to a process for producing the impregnated salts and the preservatives, and to the use of the salts and preservatives for the treatment of human and animal food, and for use in silage.

Short-chain organic acids such as formic acid, acetic acid or propionic acid are used for acidifying and preserving human and animal food. Disadvantages of these acids are, for example, their liquid state of aggregation at room temperature, the sharp or pungent odor resulting from the low vapor pressure, and their corrosiveness.

In addition, the liquid organic acids can be incorporated in concentrated form, for example into animal food, only with considerable technical complexity.

DE 28 33 727 A1 discloses a particulate fungicidal material which comprises propionic acid and a carrier material. It is said that with this material there is no increase in the number of mold colonies on stored agricultural harvest products even after incubation for several days. However, it has emerged that material of this type is itself not stable on storage (loss of acid), and the maximum amount of propionic acid which can be applied depends greatly on the carrier material used. In addition, unpleasant odors arise with this material owing to evaporation of the propionic acid.

EP-A-0 590 856 and EP-A-0 608 975 disclose mixtures of solid carboxylic acid salts and solid carboxylic acids with a lower pKa than the carboxylic acid in the salts used. When this mixture is dissolved in water, the carboxylic acids are liberated from the salts by the carboxylic acid with the lower pKa in a displacement reaction. The resulting new salts with the carboxylic acid with the lower pKa are advantageously insoluble in water and precipitate from the solution. A disadvantage of these mixtures

is that it is still necessary to use various carboxylic acids with different pKa values for producing the preservatives. In order to ensure that the carboxylic acids are completely liberated from the initial carboxylic acid salts (for example from calcium propionate) on dissolving in water, the carboxylic acids with the lower pKa (for example maleic acid) must be added in at least equimolar amounts based on the carboxyl groups present in the acids. This limits the individual carboxylic acid active substance content. If insoluble carboxylic acid salts are formed in this liberation, they must additionally be removed in a subsequent reaction.

It is an object of the present invention to provide novel compositions for treating human and animal food which do not have the abovementioned disadvantages and can easily be mixed by the user without difficulty into the human and animal food to be treated. The main aim was to produce a solid composition which has a maximum active substance content and displays very little odor, if any. The solid final product should have good storage, flow and processing properties.

We have found that this object is achieved by the novel impregnated salts comprising at least one salt of one or more carboxylic acids, which salt has been impregnated with from 0.5 to 30% by weight, based on the carboxylic acid salt, of at least one liquid carboxylic acid.

The invention additionally relates to preservatives comprising an impregnated salt of the abovementioned composition. In addition, the preservatives may advantageously comprise at least one carrier and/or formulation auxiliary and, where appropriate, be coated with a protective agent and/or dusting powder.

The invention furthermore relates to a process for producing the impregnated salts, which comprises impregnating at least one salt of a carboxylic acid or of a mixture of carboxylic acids with at least one liquid carboxylic acid until the concentration is 30% by weight based on the carboxylic acid salt.

The invention additionally relates to the production of preservatives comprising an impregnated salt of the abovementioned composition, which comprises impregnated salts comprising at least one salt of one or more carboxylic acids, which salt has been impregnated with from 0.5 to 30% by weight of at least one liquid carboxylic acid being mixed where appropriate with at least one carrier and/or at least one formulation auxiliary, and being agglomerated with or without addition of one

or more binders, and subsequently the preservatives advantageously being provided with a protective agent which solidifies at room temperature (23°C), the protective agent being added in an amount such that the resulting preservatives are coated and, where appropriate, further odorization is effected by, for example, adding fragrances. The preservatives produced in this way may advantageously also be coated with a finely dispersed dusting powder to improve the flow properties of the preservatives.

The novel impregnated salts or preservatives have the advantage that the highly pungent odor of the acid is reduced. The impregnated salts advantageously comprise an active substance content of from 68 to 75% by weight, preferably 70 to 73% by weight, particularly preferably 70 to 72% by weight, as total based on the total amount of carboxylic acids present in the salt and added. Both the novel impregnated salts and the preservatives release the acid content efficiently and rapidly from the solid and have good storage, flow and processing properties.

Liquid organic acids suitable for impregnating the carboxylic acid salts are acids or mixtures of acids which are liquid or become liquid at the processing temperatures, preferably down to 40°C or below.

C_1-C_8-mono- and/or dicarboxylic acids and the salts of these C_1-C_8-mono- and/or dicarboxylic acids are advantageously used to produce the impregnated salts or to produce the preservatives. Alkali metal, alkaline earth metal or ammonium salts are suitable. Acids such as formic, acetic and/or propionic acid and their ammonium, calcium, lithium, sodium, magnesium and/or potassium salts are preferably used. The calcium, sodium or ammonium salts are advantageously used. However, also suitable in principle are other acids such as amino acids, hydroxy carboxylic acids, oxo acids or mineral acids such as HCl or H_2SO_4 and their salts, with mineral acids being less preferred. It is possible to use single salts or mixtures of different salts of one carboxylic acid or several carboxylic acids which have been impregnated with one or more acids to produce the impregnated salts. The impregnated salts advantageously consist of the salts of a carboxylic acid which have been impregnated with the same carboxylic acid. The impregnated salts preferably consist of the salt of a carboxylic acid which has been impregnated with the same carboxylic acid. Salts of formic acid and/or propionic acid which have been impregnated with formic acid and/or propionic acid in a form which is as concentrated as possible, for example with 99% strength formic acid, are particularly preferred.

Impregnated salts produced from formic acid and the salts of formic acid are very particularly preferred.

X-Ray structural analysis of the novel impregnated salts shows an additional band by comparison with normal carboxylic acid salts.

The impregnated salts can, to improve handling, advantageously be mixed with other substances, for example with a carrier, and/or be dusted with a dusting powder.

The term impregnation means applying at least one carboxylic acid, which is liquid at 40°C or below, to the solid carboxylic acid salt(s) so that the liquid carboxylic acid(s) penetrate(s) into the salt crystal(s). As a rule, this takes place with slight evolution of heat. For the impregnation, at least one carboxylic acid is applied in an amount of up to 30% by weight, based on the carboxylic acid salt(s), onto the salt(s), preferably applying the carboxylic acid(s) in an amount of from 0.5 to 30% by weight, particularly preferably applying from 15 to 25% by weight, very particularly preferably applying from 15 to 20% by weight, based on the salt component, to produce a solid substance as reaction product. With more than 30% by weight of acid, the salt crystals start to stick together; under these conditions, free carboxylic acid is present to some extent in addition to the impregnated salts. These crystals which are stuck together can be separated from one another by adding a release agent, and the free carboxylic acid can be taken up by the release agent. With more than 35% by weight of acid, the products stick together so strongly that a pasty texture results as a consequence of the free carboxylic acid. These pasty textures can be processed to granules for example in another working step by addition of a release agent and treatment in, for example, a mixer. Since further working steps and larger amounts of a release agent are necessary if more than 30% by weight of free acid is added, these embodiments are less preferred for economic reasons. However, it is possible in principle to improve the flow properties of the impregnated salts by adding small amounts of a release agent even with less than 30% by weight of carboxylic acid. Examples of suitable and advantageous release agents are Sipernats, Aerosils and/or Tixosils.

Thus, in the novel process for producing the impregnated salts, at least one salt of a carboxylic acid or of a mixture of carboxylic acids is impregnated with at least one carboxylic acid which is liquid at 40°C or below until the concentration is 30% by weight based on the carboxylic acid salt(s).

It is also possible in the novel process for producing the impregnated salts to add at least one salt of one or more carboxylic acids to at least one carboxylic acid. This mode of production is less favorable than addition to the salt(s) so that under these conditions, for example when a mixer is used for production, an increased energy input is necessary.

The novel process for producing impregnated salts is advantageously carried out at a temperature determined by the solidification point of the carboxylic acid used. The process is carried out at from 0 to 60°C, preferably from 15 to 50°C, particularly preferably from 20 to 40°C.

In a preferred embodiment, the novel salt also has a protective agent and/or dusting powder on the surface of the crystals. The size of the impregnated salt crystals is preferably below 2.5 mm, particularly preferably from 10 µm to 2000 µm, very particularly preferably from 300 µm to 1500 µm.

The novel preservatives mean preservatives comprising impregnated salts which comprise at least one salt of one or more carboxylic acids and have been impregnated with at least one liquid carboxylic acid. These impregnated salts can be mixed in the preservatives with one or more carriers and/or formulation auxiliaries. It is possible in the novel process for producing the preservatives to agglomerate this mixture with or without addition of binder. It is then possible to apply to these preservatives a protective agent which is soluble or swellable in water at 20°C and/or a finely dispersed dusting powder so that the novel preservatives have a coating of a protective agent and/or dusting powder.

Carriers which can be employed are porous, organic or inorganic carrier materials whose particle sizes are from 1 µm to 1,000 µm, preferably from 5 µm to 100 µm.

Suitable in principle for producing such free-flowing, reduced odor agglomerates are all known organic or inorganic porous carriers as long as they are resistant to acid. Examples are cereal brans, perlite, clay materials, silicates and silicas, with inorganic carriers being preferred because their properties can be controlled better.

Examples of other carriers which can be used are diatomaceous earth, crushed sand, clay, nylon powder, insoluble metal oxides or insoluble metal salts, Aerosil, corundum, ground glass, granite, quartz or flint, aluminum phosphate, kaolin, bentonite,

zeolites, calcium silicate, talc, titanium oxide, active carbon or bonemeal.

Carriers which are preferably used are cereal brans, silicates, perlite or silicas in amounts of from 10% to 70%, preferably 20 to 40%, of the weight of the impregnated salt.

Suitable binders in the novel process are water and/or synthetic or natural polymers, for example albumin, casein, soybean protein, starch, synthetic cellulose derivatives such as carboxymethylcellulose, methylcellulose, hydroxymethyl-, hydroxyethyl- and/or -propylcellulose, polyethylene glycol, polyvinyl alcohol, polyvinylpyrrolidone, gelatin, carrageenan, chitosan, dextrin, alginates, agar-agar, gum arabic, tragacanth or guar gum, or mixtures thereof.

Protective agents which can be used are water-soluble polymers such as synthetic or natural polymers, for example gelatin, carrageenan, alginates or polyvinyl pyrrolidone, organic acids, their salts or low-melting inorganic salts.

Protective agents which are preferably used are polyethylene glycols, polyvinylpyrrolidones or C_3-C_{14}, preferably C_3-C_6, organic acids and their salts, in particular citric acid, fumaric acid, succinic acid, adipic acid, benzoic acid and their salts, or amino acids and their salts.

In a preferred embodiment of the novel process for producing the preservatives, the carboxylic acid salt is introduced into a mixer, impregnated with the organic acid, a carrier is admixed where appropriate, and subsequently agglomeration and coating with the protective agent are carried out in the presence or absence of a binder.

The impregnated salts and/or carrier particles are mixed with the protective agent, the latter ordinarily consisting of a highly concentrated solution or melt of substances which are soluble or swellable in water and solidify at room temperature (23°C). This protective agent is preferably applied in the heated state to the impregnated salt and/or carrier particles and mixed with the latter. During this, the protective agent solidifies on the surface of the impregnated salts and/or carrier particles. Suitable mixer operating parameters result in agglomeration of different particles to larger granules.

The size of the granules can be adjusted by processing parameters, for example during the mixing or during the fluidized

bed granulation, and by the amount and type of binder or else by subsequent screening or grinding. The granules preferably have an average diameter of less than 3 mm, in particular of 0.3 - 1.3 mm. It is possible where appropriate for residual water to be present in the protective agent used for coating and agglomeration. After the agglomeration process or directly after production of the impregnated salts, residual water can be bound by a dusting process with a dry and finely dispersed dusting powder. It is possible by this dusting process also to prevent the agglomerates or impregnated salts sticking together later and, in addition, to apply, for example, the salt of the organic acid used (eg. sodium or calcium formate or propionate) to the agglomerate or the salts. It is furthermore possible where appropriate to add a fragrance or flavoring, eg. vanillin, tecu flavor, citral or fructin, which makes it possible to achieve an additional odor-masking effect which, for example, makes the food attractive for animals to consume.

Protective agents which are preferably employed, such as binder liquids, are substances which are soluble or swellable in water and which solidify at room temperature. This makes it possible to dispense with a subsequent drying step in which, apart from a solvent or the additional water, part of the organic acid would also evaporate.

Particularly suitable protective agents for the agglomeration process and the coating are those which have a softening temperature above 30°C, preferably above 60°C, in order to avoid deformation of the agglomerates if the storage temperature is relatively high. The protective agents which are preferably used additionally do not counteract the pH-lowering effect of the adsorbed organic acid or even, where appropriate, assist or enhance the latter.

Examples of suitable protective agents are highly concentrated, hot sugar solutions or alkali metal/alkaline earth metal formate/ acetate/propionate solutions. The residual water content thereof can be caken up by the final dusting step. Low-melting polyethylene glycols such as PEG 4000, melts of citric acid, of adipic acid, fumaric acid or benzoic acid or their salts, highly concentrated solutions of amino acids or mixtures of these acids are suitable and preferred as binder liquids. The amount of binder liquid used is from 0.5 to 80%, preferably 10 to 25%, but particularly preferably 5 to 15%, of the weight of the granules.

Suitable dusting powders are, besides the porous carrier materials themselves, finely disperse, ground organic acids or

their salts, eg. sodium formate, and inorganic salts, Sipernats, Tixosils or Aerosils. The amounts of dusting powders added are 10%, preferably from 0.1 to 5% by weight.

In general, at least one salt of one or more organic acids is introduced into a mixer, eg. an Eirich mixer, and impregnated with at least one organic acid with low energy inputs. However, the process can also be such that the liquid is introduced into the mixer, and the salts of the carboxylic acids are metered in. Higher energy inputs are necessary in the latter case.

Care must be taken to ensure uniform impregnation and to avoid excessive local moistening, which leads to lump formation. After the impregnation, the mixer contains a free-flowing carboxylic acid salt in the form of a crystalline solid. The viscosity of the binder liquid which is subsequently metered in where appropriate should be adjusted, by appropriate selection of the temperature, so that it is below 1000 mPas, preferably < 100 mPas, in order to achieve a fine drop size distribution in the spraying. In this preferred embodiment, owing to the temperature difference between the hot binder liquid and cooler impregnated salt, the drops of binder liquid initially solidify rapidly. As the agglomeration process progresses, the temperature of the bed increases owing to the mechanical and thermal energy input by from 10 to 30°C, depending on the nature of the binder liquid. Further drops of binder liquid become attached to the previously formed agglomerates, and some of them coalesce together. The energy input increases during the agglomeration.

It is possible finally to add an odorizing agent along with the dusting powder as described above. Suitable for this in principle are a large number of fragrances and flavorings which can be selected depending on the subsequent use of the agglomerate. The content of these fragrances can be < 1%, preferably from 0.05 to 0.5%, of the weight of the granules. The agglomerates produced in this way contain little dust and have a reduced odor, and their organic acid content is readily soluble in water.

The novel inpregnated salts and/or preservatives are suitable for acid treatment and/or preservation of human and animal foods, for use in silage or for leather treatment. Human and animal foods mean, in particular, grass, agricultural crops and/or compounded animal food and the materials used to produce them, such as hay, barley, wheat, oats, rye, corn, rice, soybeans, sugarcane residues, sugarcane, rapeseed, peanuts, sunflower seeds, buckwheat chaff, silage, wet grains, pulse or grain crops, but also milk replacer, liquid, compound and mineral feeds, fish

silage or fish, meat or bone meal.

The novel preservatives may also contain other additives such as minerals, vitamins, antibiotics or protein additives. The preservatives may, in particular, contain other additives with fungicidal or bactericidal properties, such as formalin, formic acid, acetic acid, propionic acid, benzoic acid, sorbic acid or bisulfites.

The novel impregnated salts and/or preservatives are advantageously added to the material to be preserved in an amount of, in each case, from 0.1 kg to 25 kg, preferably from 0.5 kg to 20 kg, particularly preferably from 5 to 15 kg, per ton of material to be preserved.

Examples

(Purity of the formic acid and propionic acid used = 99%)

A. Formic acid

Example 1

100 g of sodium formate were introduced into a household mixer (Braun), and 15% by weight of formic acid were added. The temperature rose from 22°C to 40°C on uptake of the acid. The resulting product (= impregnated salt) was free-flowing and odorless.

Example 2

100 g of calcium formate were introduced into a household mixer, and 15% by weight of formic acid were added. The resulting product had a slightly pungent odor of formic acid and showed cohesive behavior, ie. the resulting impregnated salt was slightly damp and not free-flowing.

Example 3

100 g of potassium formate were introduced into a household mixer, and 10% by weight of formic acid were added. The temperature rose from 23°C to 45°C on uptake of the acid. The impregnated salt had a slightly pungent odor and showed a slight tendency to become granular.

B. Propionic acid

Example 4

100 g of fumaric acid were introduced into a household mixer, and 15% by weight of propionic acid were added. The product was highly cohesive and had an intense odor.

Example 5

100 g of sodium formate were introduced into a household mixer, and 15% by weight of propionic acid were added as in the previous examples. The product is highly cohesive and has an intense odor.

Example 6

100 g of calcium formate were introduced into a household mixer, and 15% by weight of propionic acid were added. The temperature rose slightly while the acid was taken up. The product had an intense odor and showed a cohesive behavior.

Example 7

100 g of calcium propionate were introduced into a household mixer, and 15% by weight of propionic acid were added. The temperature rose from 23°C to 29°C on uptake of the acid. The product is free-flowing and has an intense odor.

C. Production of preservatives

Example 8

1000 g of sodium formate were introduced into an Eirich mixer (RO2) and impregnated with 15% by weight of formic acid. 200 g of sodium formate melt at 80°C are sprayed as binder from a heated storage container through a two-component nozzle onto 1000 g of this mixture into the mixing chamber. The resulting agglomerates are dusted with 44 g of Sipernat® (= highly disperse silica supplied by Degussa). The resulting product is free-flowing and odorless.

Example 9

1000 g of sodium formate were introduced into an Eirich mixer and impregnated with 15% by weight of formic acid. For agglomeration and coating, 180 g of a concentrated glucose

solution at 80°C are sprayed as binder from a heated storage container through a two-component nozzle into the mixing chamber. The resulting agglomerates are dusted with 45 g of Sipernat® and 12 g of citral. The acid content is then 59.5%. The resulting agglomerates are free-flowing.

Example 10

As in Example 9, 500 g of sodium formate were introduced into an Eirich mixer and impregnated with 15% by weight of formic acid. Then 500 g of perlite were added. 260 g of citric acid melt at 170°C are sprayed in as binder from a heated storage container through a two-component nozzle into the mixing chamber. The resulting agglomerates are dusted with 44 g of Sipernat® and 8 g of vanillin. The total acid content is 29.7%. The resulting preservatives are free-flowing and odorless. The impregnated salts described in Examples 1 to 7 can also be converted as in Examples 8 to 10 into free-flowing preservatives with a reduced odor or no odor.

The following Examples 11 to 14 show storage stability tests for an impregnated salt (sodium formate impregnated with 20% by weight formic acid) treated with various protective agents and/or dusting powders (see Table 1). Part-quantities of the impregnated salts were placed in a tumbler mixer and mixed for a further 10 min while adding the additives (see Table 1). The products were then introduced into a steel vessel (diameter about 40 mm) up to 15 - 20 mm below the rim of the vessel and stored in a drying oven at 35°C under load (simulated with a metal piston), the load corresponding to simulated storage under normal storage conditions, and tested at the stated times. Because of the small diameter of the test vessel and the storage under pressure, in order to establish whether a product is free-flowing or not, it is necessary to tap the vessel. The terms used to indicate the result of the flow test have the following meanings:
gentle tapping 1x, gentle tapping 2x and tapping 1x = product is free-flowing
tapping 3x = product shows caking but is essentially free-flowing
tapping 4x, tapping 5x and tapping >5x = product is caked and essentially no longer free flowing.

Table 1: Storage stability of the impregnated salts

Example	Storage time in days	Additive	Flow test	Remarks
11	7 d	1% FK500LS[1]	tapping 1x	slightly caked, loose
		2% FK500LS	tapping 1x	no caking
		4% FK500LS	gentle tapping 1x	no caking
		1% Sip.50S[2]	gentle tapping 2x	caked
		2% Sip.50S	gentle tapping 1x	no caking, dust
		4% Sip.50S	gentle tapping 1x	no caking, dust
12	14 d	1% Aerosil200[3]	tapping 3x	caked
		2% Aerosil200	tapping 2x	slightly caked
		3% Aerosil200	tapping 1x	no caking
		4% Aerosil200	-	
		5% Aerosil200	tapping 2x	no caking, dust
		2% Aerosil200 + 2% D17[4]	tapping 2x	no caking, much dust
		2% D17	tapping 1x	slight caking, dust
		5% D17	tapping 1x	no caking, dust

Example	Storage time in days	Additive	Flow test	Remarks
13	7 d	2% R972[5] + 2% benzoic acid	tapping >5x	very caked
		2% R972 + 2% Na benzoate	tapping >5x	very caked
		2% R972 + 2% K sorbate	tapping >5x	very caked
		4% R972	tapping 4x	caked
		2% R972 + 1% FK500LS	tapping 1x	no lumps
		2% R972 + 2% FK500LS	tapping 1x	dust, no lumps
		2% R972 + 2% Zeolite[6]	tapping 5x	very caked
		2% R972 + 2% sorbitol	tapping >5x	very caked
14	7	1% Aerosil200	tapping 3x	caked
		2% Aero-sil200	tapping 2x	slightly caked
		3% Aero-sil200	tapping 1x	slightly caked
		4% Aero-sil200	tapping 3x	not caked, dust
		5% Aero-sil200	tapping 3x	not caked, dust
		2% cornmeal	tapping >5x	very caked
		5% cornmeal	tapping >5x	very caked
		2% D17	tapping 1x	slightly caked
		2% D17	tapping 1x	not caked, dust
		1% Aero-sil200 + 2% R972	tapping 1x	not caked
		2% Aero-sil200 + 2% R972	tapping 1x	slightly caked, dust

[1,2,3,4,5] various silicas supplied by Degussa

[6] Zeolite supplied by Degussa

D. Acidification of foodstuffs

Example 15

A piglet starter feed was treated with 10 kg/t or 20 kg/t of an impregnated salt (sodium formate/15% by weight formic acid). The pH of the feed fell from 6.4 to respectively 5.5 or 5.1.

We claim:

1. Impregnated salts comprising at least one salt of one or more carboxylic acids, which salt has been impregnated with from 0.5 to 30% by weight, based on the carboxylic acid salt, of at least one liquid carboxylic acid.

2. Impregnated salts as claimed in claim 1, comprising at least one salt of a C_1-C_8-mono- or dicarboxylic acid, which salt has been impregnated with at least one C_1-C_8-mono- or dicarboxylic acid.

3. Impregnated salts as claimed in claim 1 or 2, comprising at least one salt of a carboxylic acid selected from the group of formic acid, acetic acid or propionic acid, which salt has been impregnated with at least one carboxylic acid selected from the group of formic acid, acetic acid or propionic acid.

4. Impregnated salts as claimed in any of claims 1 to 3, where the carboxylic acids in the carboxylic acid salts and the carboxylic acid used for impregnating the salts are identical.

5. Impregnated salts as claimed in any of claims 1 to 4, wherein the impregnated salts comprise at least one salt of one or more carboxylic acids selected from the group of ammonium, potassium, sodium, lithium, magnesium or calcium salts.

6. A preservative comprising an impregnated salt as claimed in claim 1.

7. A preservative as claimed in claim 6, additionally comprising a carrier and/or formulation auxiliaries.

8. A preservative as claimed in claim 6 or 7, which is coated with a protective agent which is soluble or swellable in water at 20°C.

9. A preservative as claimed in any of claims 6 to 8, wherein water-soluble polymers, organic acids, their salts or low-melting inorganic salts are used as protective agents.

10. A preservative as claimed in any of claims 6 to 9, wherein polyethylene glycols, polyvinylpyrrolidones or C_3-C_{14}, preferably C_3-C_6, organic acids and their salts, in particular citric acid, fumaric acid, succinic acid, adipic acid,

benzoic acid, sorbic acid and their salts, or amino acids and their salts, are used as protective agents.

11. A preservative as claimed in any of claims 6 to 10, wherein a dusting powder is applied to the surface in addition to or in place of the protective agent.

12. A process for producing impregnated salts as claimed in claim 1, which comprises impregnating at least one salt of a carboxylic acid or of a mixture of carboxylic acids with at least one liquid carboxylic acid until the concentration is 30% by weight based on the carboxylic acid salt.

13. A process as claimed in claim 12, wherein at least one carboxylic acid is introduced into a mixer, and at least one salt of a carboxylic acid or of a mixture of carboxylic acids is metered in.

14. A process for producing a preservative as claimed in claim 6, which comprises mixing impregnated salts as claimed in claim 1 with one or more carriers and/or formulation auxiliaries, and agglomerating with or without the addition of at least one binder.

15. A process as claimed in claim 14, wherein the preservative is coated with a protective agent which is soluble or swellable in water at 20°C and/or if required the flow characteristics of the preservative are ensured by dusting with a finely dispersed dusting powder.

16. The use of the impregnated salts as claimed in claim 1 or of the preservative as claimed in claim 6 for acid treatment, for preserving human and animal food, or for use in silage or for leather treatment.

Impregnated salts, their production and their use

Abstract

The present invention relates to impregnated salts comprising at least one salt of one or more carboxylic acids, which salt has been impregnated with from 0.5 to 30% by weight, based on the carboxylic acid salt, of at least one carboxylic acid, and to preservatives comprising an impregnated salt and, where appropriate, at least one carrier and/or formulation auxiliaries, it being possible for the preservatives to be coated with a protective agent and/or a dusting powder.

The invention furthermore relates to a process for producing the impregnated salts and the preservatives, and to the use of the salts and preservatives for the treatment of human and animal food, and for use in silage or for leather treatment.

Declaration, Power of Attorney

0050/048320

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Impregnated salts, their production and their use

the specification of which

[ ] is attached hereto.

[ ] was filed on _____ as

Application Serial No. _____

and amended on _____.

[x] was filed as PCT international application

Number PCT/EP 98/05469

on 28/08/1998

and was amended under PCT Article 19

on _____ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above–identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)–(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	**Country**	**Day/Month/Year**	**Priority Claimed**	
19739319.5	*Germany*	*08 September 1997*	[x] Yes	[ ] No

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

_____ (Application Number) _____ (Filing Date)

_____ (Application Number) _____ (Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	**Filing Date**	**Status (pending, patented, abandoned)**

And we (I) hereby appoint **Messrs. HERBERT. B. KEIL**, Registration Number 18,967; and **RUSSEL E. WEINKAUF**, Registration Number 18, 495; the address of both being Messrs. Keil & Weinkauf, 1101 Connecticut Ave., N.W., Washington, D.C. 20036 (telephone 202–659–0100), our attorneys, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to sign the drawings, to receive the patent, and to transact all business in the Patent Office connected therewith.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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